Biocidal Polyester

JIAN LIN,[1] CATHERINE WINKELMANN,[1] S. D. WORLEY,[1] JANGHO KIM,[2] C-I. WEI,[2] UNCHIN CHO,[3] R. M. BROUGHTON,[3] J. I. SANTIAGO,[4] J. F. WILLIAMS[4]

[1] Department of Chemistry, Auburn University, Auburn, Alabama 36849

[2] Department of Nutrition and Food Science, Auburn University, Auburn, Alabama 36849

[3] Department of Textile Engineering, Auburn University, Auburn, Alabama 36849

[4] Halosource Corporation, Seattle, Washington 98121

Received 17 September 2001; accepted 24 September 2001

ABSTRACT: Polyester fabrics were modified by covalently linking heterocyclic moieties, which could be halogenated, to the surfaces of the polyester fibers. Antimicrobial activity was introduced into the fabrics and fibers by exposure to a source of oxidative chlorine (chlorine bleach) that converted the heterocyclic precursor moieties into N-chloramine functionalities. The antimicrobial activity could be repeatedly regenerated following its loss on challenge with suspensions of bacteria by further washing with aqueous oxidative chlorine. Biocidal polyester fabrics, fibers, and other materials potentially will be effective in reducing, or eliminating entirely, pathogenic microorganisms and odor-causing micro-organisms which directly contact them. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 177–182, 2002

Key words: polyester; biocidal polymer; N-halamine

INTRODUCTION

A very desirable property to be introduced into textile fabrics is antimicrobial activity for the obvious uses in medical applications, as well as for reducing noxious odor in clothing, carpets, hygienic pads, and air filters. A considerable amount of research effort has been expended in recent years in attempts to render the polymers employed in manufacturing textile products biocidal. Most efforts have involved the use of coating, grafting, impregnation, and blending technologies which can yield antibacterial, or at least bacteriostatic, properties. However, it is common with these technologies that the biocidal function is short-lived and nonregenerable upon exposure to multiple wash cycles or to reactive chemicals. The optimum biocidal textile should be one in which the biocidal functionality is imparted to the host polymer through an irreversible chemical reaction to produce covalent bonds without causing significant deterioration of the desirable and necessary properties of the host polymer. If the biocidal property is lost over a period of time due to inherent instability, then it is important that it can be restored through some type of regeneration process.

A biocidal functionality for polymers that satisfies the requirements mentioned above is the

Correspondence to: S. D. Worley (worlesd@auburn.edu).

Contract grant sponsor: U.S. Department of Commerce; contract grant number: 99-27-07400.

Contract grant sponsor: U.S. Air Force; contract grant number: F08637-01-C-6004.

Contract grant sponsor: Halosource Corporation.

Journal of Applied Polymer Science, Vol. 85, 177–182 (2002)

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
14-APR-2006	Journal Article POSTPRINT	01-AUG-2000 -- 31-AUG-2001

4. TITLE AND SUBTITLE

Biocidal Polyester

5a. CONTRACT NUMBER

F08637-02-C-7020

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Lin, Jian; Winkelmann, Catherine; Worley, S.D.; Jangho, Kim; Wei, C-I; Cho, Unchin; Broughton, R. M.; Santiago, J. I.; Williams, J. F.

5d. PROJECT NUMBER

ARMT

5e. TASK NUMBER

00

5f. WORK UNIT NUMBER

ARMT0048

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry
Auburn University
Auburn AL 36849

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory
Materials and Manufacturing Directorate
Airbase Technologies Division
139 Barnes Drive, Suite 2
Tyndall Air Force Base, FL 32403-5323

10. SPONSOR/MONITOR'S ACRONYM(S)

AFRL/RXQL

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

AFRL-RX-TY-TP-2005-4595

12. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution Statement A: Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

Reprinted from J. Appl. Polym. Sci., 85 (2002) 177-182

14. ABSTRACT

Polyester fabrics were modified by covalently linking heterocyclic moieties, which could be halogenated, to the surfaces of the polyester fabrics. Antimicrobial activity was introduced into the fabrics and fibers by exposure to a source of oxidative chlorine (chlorine bleach) that converted the heterocyclic polymer moieties into N-chloramine functionalites. The antimicrobial activity could be repeatedly regenerated following its loss on challenge with suspensions of bacteria by further washing with aqueous oxidative chlorine. Biocidal polyester fabrics, fibers, and other materials potentially will be effective in reducing, or eliminating entirely, pathogenic microorganisms and odor causing microorganisms which directly contact them.

15. SUBJECT TERMS

antimicrobial, biocide, bleach, chlorine, polyester, sterilize

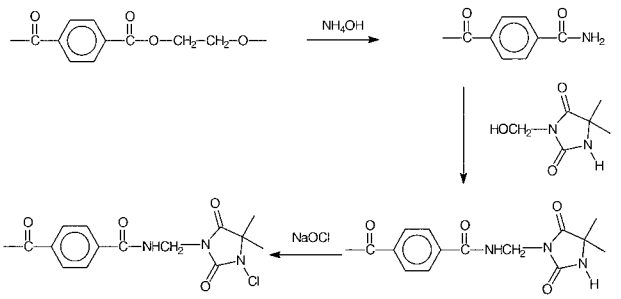
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(Include area code)*
U	U	U	UU	7	

Reset

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

cyclic N-halamine moiety. Extensive work in these laboratories over the past decade[1] has established that N-halamine groups such as N-halo hydantoins, oxazolidinones, and imidazolidinones can be covalently attached to a variety of polymers used in water disinfection applications,[2–4] surface coatings,[5–7] and elastomers.[8] Sun and coworkers, in pioneering work on textile fabrics, have extended the technology to its use in rendering fabrics containing cellulose (cotton and cotton blends) biocidal.[9,10] More recently, it has been demonstrated that nylon can also be rendered biocidal with similar technology.[11,12] As will be discussed herein, it is now evident that poly(ethylene terephthalate), PET, can also be functionalized with a biocidal N-halamine moiety utilizing similar chemistry to that employed for cellulose and nylon.

Several recent reports concerning the introduction of an antibacterial functionality into PET have appeared. Buchenska has shown that some antibacterial activity can be imparted to PET fibers that have been grafted with acrylic acid and subsequently treated with antibiotics; the antibiotics are slowly released into solutions.[13] Kang and coworkers have produced chitosan-grafted and quaternized chitosan-grafted PET following a glow-discharge graft of acrylic acid onto the PET; the treated PET was able to inhibit the growth of bacteria after long contact times (6 h).[14] Yang and coworkers have treated 100% polyester fabric in a range finishing and batch exhaustion process with 2-hydroxy-2′,4,4′-trichloro-diphenyl ether, and showed the treated fabric to have weak bactericidal efficacy against *Staphylococcus aureus* and *Escherichia coli* before and after multiple washes.[15] Sun and coworkers have recently demonstrated that the novel monomers 3-allyl-5,5-dimethylhydantoin and 1-acryloyl-2,2,5,5-tetramethylimidazolidin-4-one can be grafted onto PET in a continuous finishing process.[16,17] Upon subsequent chlorination, the resulting fabrics containing the N-chloramine functionality become biocidal, and can withstand multiple washing cycles while retaining activity. More important, once activity is lost, the treated PET can be rechlorinated and regain its biocidal efficacy.[16,17] The present study will demonstrate an alternate means of creating the N-halamine biocidal functionality on PET. A portion of the PET chains on the surface of the fibers will be interrupted through alkaline hydrolysis in aqueous ammonia, followed by reaction of the resulting amide fragments with 3-hydroxymethyl-5,5-dimethylhydantoin, and subsequent chlorination with sodium hypochlorite (Scheme 1). It will be demonstrated that the resulting treated PET is bactericidal and capable of being regenerated once the initial chlorine charge is exhausted.



Scheme 1 The reaction sequence used in producing the biocidal PET fabric.

EXPERIMENTAL

Treatment Process

Square swatches (3 × 3 in) of PET fabric (100% Dacron Type 54 purchased from Test Fabrics, Inc., Middlesex, NJ) were washed according to American Association of Textile Chemists and Colorists (AATCC) Test Method 124 before use. The cleaned swatches were soaked in saturated ammonium hydroxide solution (29.6%) at 34°C for a variable time of 0.5 to 3.0 h followed by three distilled water rinses. A treating bath was prepared that contained 5.0 g of MDMH (a mixture of 3-hydroxymethyl-5,5-dimethylhydantoin and 1-hydroxymethyl-5,5-dimethylhydantoin; Dantoin® purchased from the Lonza Chemical Company, Fairlawn, NJ), 0.6 g of magnesium chloride as a catalyst, 0.2 g of Triton X-100 as a wetting agent, and 100 mL of distilled water. The pH of the bath was adjusted to 2.5 with 1% sulfuric acid solution. The fabric swatches were soaked in the bath at 80°C for 30 min. After drying in air, they were cured at 140°C for 2.0 h under a nitrogen atmosphere. Then they were washed with chlorine demand-free (CDF) water. The swatches were rendered biocidal by soaking in a solution of free chlorine (50% Clorox®), which contained 2.6% of sodium hypochlorite for a variable time of 5 min to 8.0 h at room temperature. Then they were rinsed with CDF water until free chlorine could not be detected in the effluent (<0.2 mg/L). Following drying in air, they were tested for antimi-

crobial efficacy. The chemical reactions used in the treatment process are shown in Scheme 1.

Biocidal Efficacy

Swatches of test and control fabrics were tested quantitatively for antibacterial activity using a modified version of AATCC Method 100. In the method, sized and shaped-treated swatches were placed in sterile Petri dishes. A known volume of inoculum containing bacteria [Gram-positive *Staphylococcus aureus* (ATCC 5368) or Gram-negative *Escherichia coli* (ATCC 2666)] at a concentration of about 10^8 CFU/mL in pH 7 phosphate buffer solution was used. For the inoculation procedure, complete absoption of the bacterial solution was required with no free solution being available. Swatches of unchlorinated, but otherwise identical fabric, were employed as controls. Each swatch was inoculated with a known volume of inoculum ensuring even distribution and, after a measured contact time, was transferred into a sterile wide-mouthed glass vessel. Following the transfer, 0.02 *N* sodium thiosulfate was added to quench further biocidal action. The vessel and contents were shaken, and an aliquot of the resulting mixture was removed. Following a set of serial dilutions with pH 7 phosphate buffer, a 0.025-mL aliquot of each dilution was plated on Nutrient agar and incubated for a period of 48 h. Bacterial counting was performed after 24 h and 48 h of incubation.

Analyses of Chlorine on Fabric

Two types of experiments were performed. In one, the biocidal PET fabric was examined for loss of chlorine during storage. In the other, the fabric was exposed to sodium thiosulfate (0.00375 *N*) so as to reduce all of the oxidative chlorine, and then it was rechlorinated several times as described in the Treatment section. A standard iodometric/thiosulfate titration procedure was employed to measure the chlorine content of the fabric. Strips of known surface area were soaked in 100 mL of distilled water containg 0.1 g of potassium iodide, 1 mL of phthalate buffer (pH 4), and 3 drops of 1% starch in a flask. The flask was sealed after purging with nitrogen gas, and the mixture was stirred at room temperature for 8 h. The resulting blue solution, containing the strips of fabric, was then titrated with standard sodium thiosulfate to a clear endpoint. The equation used to calculate the mg of Cl on the surface of the fabric is:

$$W_{Cl} = (V \times N \times 35.45)/(S \times 2) \quad (1)$$

where W_{Cl} is the mg/cm^2 of Cl bonded to the surface of the fabric, V and N are the volume and normality, respectively, of the sodium thiosulfate, and S is the surface area in cm^2 of the swatch.

Tensile Strength Test

An Instron Model 1122 Tensile Tester was employed to determine the maximum load and percent elongation of the treated PET fibers upon reaching the point of breakage. A total of 10 one-inch fibers were tested for each sample with the results averaged. The tests were conducted at 21°C and 65% relative humidity. The full-scale load on the constant-rate-of-extension Instron was 50.0 lbf, and the crosshead speed employed was 10 in/min. The samples were treated with ammonium hydroxide for 0.5 h, 1.0 h, 1.5 h, 2.0 h, and 3.0 h, corresponding to samples PETH-1, PETH-2, PETH-3, PETH-4, and PETH-5 in Table VI. "PET" refers to poly(ethylene terephthalate); "H" refers to subsequent treatment with MDMH. The samples tested were not chlorinated.

RESULTS AND DISCUSSION

The key reaction step in the conversion of PET fabric into a form that can be rendered bactericidal is the formation of amide fragments on the surfaces of the fibers. This was accomplished by hydrolysis of a portion of the PET ester linkages and subsequent reaction with ammonia. The hy-

Table I Antibacterial Swatch Testing after Different Contact Times

Sample[a]	Contact Time (min)[b]	Antibacterial Performance (Log Reduction)
PETHCl	30	6.9
PETH	30	1.9
PETHCl	20	6.6
PETH	20	1.9
PETHCl	10	5.3
PETH	10	0.9
PETHCl	5	4.3
PETH	5	2.0

[a]"Cl" indicates a chlorinated sample having antibacterial activity; absence of "Cl" indicates an unchlorinated control.

[b]The challenge of *S. aureus* was 1.3×10^9 CFU (9.1 logs) per 6.45 cm^2 swatch.

Table II Antibacterial Swatch Testing after Variable Times of Dry Storage

Sample	Time after Preparation (Days)	Challenge of *S. aureus* (Log)[a]	Microbiological Performance (Log Reduction)
PETHCl	1	8.4	8.4
PETH	1	8.4	0.0
PETHCl	3	8.3	8.3
PETH	3	8.3	1.2
PETHCl	7	9.0	6.8
PETH	7	9.0	0.3
PETHCl	14	9.0	6.8
PETH	14	9.0	0.2

[a]The challenge contact time was 60 min.

drolysis step can be effected with other bases such as dilute sodium hydroxide, followed by exposure to ammonium hydroxide to form the amide fragments. However, ammonium hydroxide works well in its dual role of inducing ester hydrolysis and formation of the amide fragments. Also, being a weak base, less fragmentation occurs with the ammonia, which leads to less deterioration of the strength of the fibers than is the case with the stronger base. Treatment of polyester fabric with alkaline solutions is already commonly employed during commercial processing. It was found that time of exposure in the bath containing the ammonium hydroxide (0.5–3.0 h) did not affect the biocidal efficacy of the fabric, nor its tensile strength, as will be discussed later. Also, it was found that variation of chlorination conditions for the treated fabric (concentration of bleach in the range 50–100%; time of chlorination in the range 5 min to 8.0 h) did not affect the biocidal efficacy.

The results in Table 1 show that when a very high challenge load of *S. aureus* (9.1 logs) was employed, the chlorinated samples showed reasonable antibacterial activity (6.9 log inactivation) at a contact time of 30 min; there was some efficacy (4.3 log inactivation) even at the shortest contact time (5 min) tested. If the contact time is extended to 60 min, an 8.5 log reduction of *S. aureus* has been observed. In a similar, but limited, study of the efficacy of the treated PET against *E. coli*, a 5.7 log reduction (100%) was observed at a contact time of 10 min, but the reduction dropped to 64% at a contact time of 5 min. The efficacy results in this study compare favorably with those obtained for PET treated with other N-chloramine functionalities,[16,17] and are much superior to those reported elsewhere for which other treatment techniques were employed.[13–15]

Tables II and III present data relevant to the stability of the chlorine bonded to the hydantoin moiety during dry storage. From Table II it is observed that the efficacy of the treated textile fabric against *S. aureus* declined only slightly (from 8.4 log inactivation to 6.8 log inactivation) over a 2-week period of storage in a sealed plastic bag at room temperature in the absence of light.

Table III Stability of Chlorine Bonded on Halamine Moiety after Dry Storage

Time of Storage (Days)	Chlorine (mg/cm^2) on Fabric
1	6.47×10^{-3}
3	5.70×10^{-3}
7	4.76×10^{-3}
14	2.98×10^{-3}

Table IV Regeneration of Antibacterial Activity

Sample	Chlorination	Microbiological Performance (Log Reduction)[a]
PETHCl-1	First: 50% Clorox®	9.0
PETH	None	0.3
PETHCl-2	Second: 50% Clorox®	9.0
PETH	None	0.2

[a]The challenge of *S. aureus* was 1.0×10^9 CFU (9.0 logs) per 6.45 cm^2 swatch for a contact time of 60 min.

Table V Chlorine on Regenerated PET Fabric

Repetitive Chlorination	Chlorine (mg/cm^2) on Fabric
1st	6.47×10^{-3}
2nd	6.00×10^{-3}
3rd	5.79×10^{-3}
4th	5.62×10^{-3}
5th	5.70×10^{-3}

The data in Table III indicate that the treated PET fabric lost about 54% of its chlorine over the 2 weeks, and that after storage for 1 day, it contained 1.10×10^{17} Cl atoms/cm^2. This chlorine loading was adequate to completely inactivate the 2.5×10^8 CFU/swatch (having surface area 6.45 cm^2) of *S. aureus* during the 60-min contact time.

Tables IV and V address the regenerative property of the biocidal PET fabric. Table IV shows that the biocidal efficacy of the treated PET could be completely recovered after being destroyed by the reducing agent sodium thiosulfate by rechlorination under the same conditions as originally employed. Table V indicates that insignificant changes in chlorine atoms/cm^2 occur over five cycles of reduction with sodium thiosulfate followed by reoxidation with chlorine bleach.

The data in Table VI were generated to test whether the ammonia treatment of the PET caused deterioration of the fibers. The standard deviations in the data were such that it can be stated that there was no significant difference between the treated fibers and the PETH control fibers, even when long-term exposure to the ammonium hydroxide solution was employed. In other words, the treatment conditions did not significantly affect the strength of the fibers. The chlorinated samples were not tested, but any significant weakening of the PETH fibers should have occurred under the ester hydrolyses conditions, i.e., under the conditions of exposure to ammonium hydroxide.

Generally the biocidal efficacies of N-halamine compounds are inversely related to the strengths of their nitrogen–halogen covalent bonds.[18] This appears to be true even for N-halamine compounds that liberate very little free halogen into aqueous solution. These compounds, with very strong N—Cl bonds are thought to inactivate pathogens by a direct contact mechanism in which the oxidative chlorine atom is transferred directly to the cell, rather than following dissociation of the N—Cl bond through hydrolysis to form "free chlorine," which then becomes the active biocide. Thus, it is conceivable that an N-halamine moiety other than the hydantoin discussed above could provide a more rapid inactivation of the pathogens, but have less shelf life, or vice versa. In fact, this notion is borne out by recent results from these laboratories. Using the N-halamine precursors 4-hydroxymethyl-4-ethyl-2-oxazolidinone and 3-hydroxymethyl-2,2,5,5-tetramethylimidazolidin-4-one, and the same treatment procedure as reported in the Experimental section for the hydantoin derivative, we have been able to produce the corresponding biocidal PET fabrics.[19] These biocidal PET fabrics require somewhat longer contact times for complete inactivation of *S. aureus* than does the hydantoin derivative, but they retain chlorine for a longer period. This is as expected, because the N—Cl bond is stronger for the oxazolidinone and imidazolidinone moieties than for the hydantoin.

Table VI Tensile Properties of PET Fibers by the Single-Strand Method

Sample[a]	Displacement at Maximum (lbf)	Strain at Maximum (%)	Tensile Strength (lbf)
PET original[b]	0.57	57	1.10
PETH-1	0.43	43	1.06
PETH-2	0.55	55	1.09
PETH-3	0.46	46	1.06
PETH-4	0.52	52	1.07
PETH-5	0.44	44	1.01

[a]The samples were treated with ammonium hydroxide for different times (see Experimental section).

[b]The sample was not treated, i.e., a control.

CONCLUSIONS

This study has demonstrated that PET fabrics can be rendered antimicrobial by chemically bonding heterocyclic N-halamine functional groups to the polyester molecule following fragmentation of a portion of its ester linkages utilizing ammonia for hydrolysis and conversion to amide fragments without significantly reducing the strengths of the fibers. The treated materials have been shown to be bactericidal against the bacteria *Staphylococcus aureus* and *Escherichia coli*. Upon loss of the antimicrobial chlorine atom, activity can be restored by exposure to a source of free chlorine such as bleach. It is anticipated that this technology will be useful in rendering such commercial products as clothing antimicrobial, and for reducing, or eliminating, noxious odors in polyester products.

This work was supported by U. S. Department of Commerce Grant 99-27-07400 to the National Textile Center, by U.S. Air Force Contract FO8637-01-C-6004 (Tyndall AFB), and by the Halosource Corporation.

REFERENCES

1. Worley, S. D.; Sun, G. Trends Polym Sci 1996, 4, 364.
2. Sun, G.; Wheatley, W. B.; Worley, S. D. Ind Eng Chem Res 1994, 33, 168.
3. Sun, G.; Allen, L. C.; Luckie, E. P.; Wheatley, W. B.; Worley, S. D. Ind Eng Chem. Res 1995, 34, 4106.
4. Sun, G.; Chen, T. Y.; Habercom, M. S.; Wheatley, W. B.; Worley, S. D. J Am Water Res Assoc 1996, 32, 793.
5. Eknoian, M. W.; Putman, J. H.; Worley, S. D. Ind Eng Chem Res 1998, 37, 2873.
6. Eknoian, M. W.; Worley, S. D. J Bioact Compat Polym 1998, 13, 303.
7. Eknoian, M. W.; Worley, S. D.; Bickert, J.; Williams, J. F. Polym 1999, 40, 1367.
8. Elrod, D. B.; Figlar, J. G.; Worley, S. D.; Broughton, R. M.; Bickert, J. R.; Santiago, J. I.; Williams, J. F. Rubber Chem Technol 2001, 74, 331.
9. Sun, G.; Xu, X. Textile Chem Col 1998, 6, 26.
10. Sun, G.; Xu, X. Textile Chem Col 1999, 31, 21.
11. Lin, J.; Winkelmann, C.; Worley, S. D.; Broughton, R. M.; Williams, J. F. J Appl Polym Sci 2001, 81, 943.
12. Lin, J.; Cammarata, V.; Worley, S. D. Polymer 2001, 42, 7903.
13. Buchenska, J. J Appl. Polym Sci 1997, 65, 967.
14. Huh, M. W.; Kang, I. K.; Lee, D. H.; Kim, W. S.; Lee, D. H.; Park, L. S.; Min, K. E.; Seo, K. H. J Appl Polym Sci 2001, 81, 2769.
15. Yang, Y.; Corcoran, L.; Vorlicek, K.; Li, S. Textile Chem Col 2000, 32, 44.
16. Sun, Y.; Sun, G. J Appl Polym Sci, to appear.
17. Sun, Y.; Chen, T. Y.; Worley, S. D.; Sun, G. Polymer, to appear.
18. Worley, S. D.; Williams, D. E. Crit Rev Environ Contr 1988, 18, 133.
19. Lin, J.; Worley, S. D.; Kim, J.; Wei, C-I., unpublished data.